XI. *The Mobilities of the Ions produced by Röntgen Rays in Gases and Vapours.*

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1. *Introductory.*

For various reasons the determination of the velocities in an electric field of the ions produced in gases by the action of Röntgen rays is of fundamental importance in electrical theory. A knowledge of the ionic mobilities (*i.e.* the velocities under unit electric intensity) affords information with regard to the structure of the ion; if, in addition, the diffusion coefficients of the ions in various gases are known, the charge associated with the ion can be compared with that carried by the monovalent ion in the electrolysis of solutions.

Experimental methods of determining the mobilities of the positive and negative ions were devised not long after the ionising action of the Röntgen rays was known. Rutherford[*] determined the values of the sum of the positive and negative mobilities in a series of gases. Zeleny,[†] by comparing the velocity acquired by the ions in an electric field with that of a gaseous current parallel to the field, succeeded in deducing the values of the difference of the ionic mobilities and also their ratio. In later experiments Zeleny[‡] employed a current of gas in a direction perpendicular to the electric field and deduced the absolute values of the mobilities in air, oxygen, carbon dioxide, and hydrogen.[§]

No determinations, however, were made of the ionic mobilities in vapours. The determination of the physical constants of vapours opened out a considerable field for

[*] 'Phil. Mag.,' vol. 44, p. 422 (1897).

[†] 'Phil. Mag.,' vol. 46, p. 120 (1898).

[‡] 'Phil. Trans.,' A, vol. 195, p. 193 (1900).

[§] For a concise account of the experiments on ionic mobilities *vide* J. J. Thomson, "Conduction of Electricity through Gases," 2nd edition.

theoretical research and afforded rich material for the application of the kinetic theory of gases. The measurement of the mobilities of the two kinds of ions formed by the action of Röntgen rays in a series of vapours seemed, therefore, to form a fitting and necessary continuation of the corresponding determinations in the case of gases; with this object in view the present research was undertaken.

2. *Experimental Method.*

The method employed throughout was that devised by LANGEVIN,[*] who measured the ionic mobilities in air over a range of pressures varying from 7·5 to 143 cm. of mercury. The principle of the method is as follows :—

Suppose we have two parallel plates A and B at a distance d apart, and let there be a uniform electric field X in the region between the plates, the force on a positive charge being from B to A. Let the gas comprised between them be ionised uniformly by a single flash of very short duration from a Röntgen-ray bulb. After the lapse of a certain time t from the passage of the Röntgen-ray discharge, let the field between A and B be suddenly reversed in direction; from this time until all the ions have been removed by the field A will receive only negative electricity.

Neglecting effects due to the recombination and diffusion of ions, the total quantity of electricity received by the plate A from the time of the Röntgen-ray discharge until all the ions are removed is given by

$$Q = \frac{Q_0}{d} (k_1 + k_2) Xt - Q_0,$$

where Q_0 = quantity of electricity of one sign liberated between the plates by the flash of Röntgen rays,

k_1 = velocity of the positive ion under unit electric intensity,

k_2 = corresponding velocity for the negative ion.

By varying the time interval t, a series of values of Q is obtained; the relation between Q and t as given by the above equation is representable by a straight line, but this equation has necessarily to be modified by the conditions :—

(i) Each of the quantities $k_1 Xt$ and $k_2 Xt$ is to be regarded as zero for negative values of t. This implies $Q = -Q_0$ for $t < 0$.

(ii) Each of the quantities $k_1 Xt$ and $k_2 Xt$ cannot numerically be greater than d. This implies $Q = Q_0$ for values of t greater than the larger of the two quantities $d/k_1 X$ and $d/k_2 X$.

With these conditions the relation between Q and t is expressed by a curve of the character given in fig. 1.

* 'Ann. de Chim. et de Phys.,' VII., 28, p. 495 (1903).

It is noticeable from the figure that this curve consists of portions of straight lines intersecting at points which have as abscissæ 0, d/k_2X, d/k_1X (for the case $k_2 > k_1$), and which correspond respectively, as far as time considerations are concerned, to the momentary Röntgen-ray discharge, the withdrawal of all the negative ions, and the receipt of all the positive ions by the plate A. It is evident that, if a curve with the above characteristic features could be obtained experimentally, we could deduce from the positions of the points the values of d/k_1X and d/k_2X and thus obtain the mobilities of the ions for the gas or vapour under consideration. This procedure would not, however, be advisable in practice. The curve in fig. 1 corresponds only to
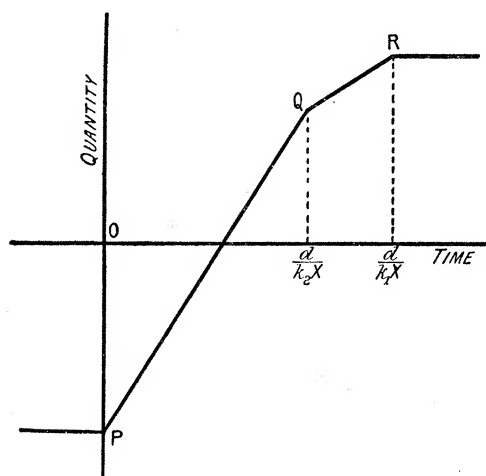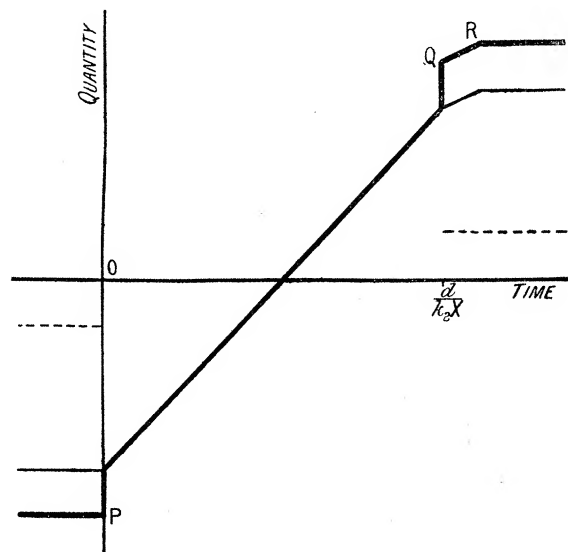

Fig. 1.   Fig. 2.

ideal conditions; as has been mentioned above, the ionisation must be uniform throughout the interval between the two plates, such uniformity being only approximately realised in practice; moreover, LANGEVIN has shown that, as a result of the recombination and diffusion of the ions, the effects of which have been neglected in the theoretical treatment, the curve as realised experimentally does not consist of separate straight lines, but of separate curves which form nicks at their points of intersection, the positions of which, however, have not been displaced.

If the ionisation consist of a uniform distribution between the plates, together with a layer of intense secondary ionisation close to the plate A, the theoretical curve expressing the relation between Q and t can readily be obtained by adding the ordinates due to each part of the ionisation. This curve is shown by the thick lines in fig. 2, the thin lines denoting the curve due to the uniform ionisation as before, and the dotted lines the curve due to the ionisation localised near the plate A.

As a result of recombination and diffusion the nicks will be rounded off; moreover, the part QR of the resultant curve is scarcely realisable in practice, especially if there be little difference in the values of the two mobilities. In fig. 3 is given the type

of curve actually obtained by experiment; it was obtained under the following conditions:—

Gas between electrodes, carbon monoxide at 1 atmosphere.

X (before reversal) = 38·7 volts per centimetre.

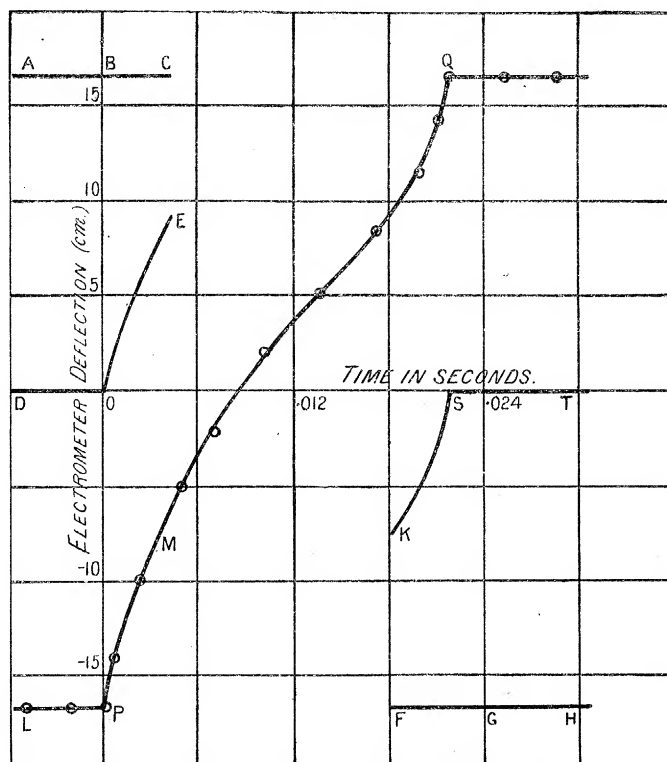Distance between electrodes, 1 cm.

Fig. 3.

In general, only two points of discontinuous curvature are noticeable, the first corresponding to the Röntgen ray discharge and the second to the withdrawal of all the ions of one sign, viz., the negative ions if B be at a positive potential before reversal and the positive ions if B be at a negative potential before reversal. By obtaining experimentally curves for the two cases of B positive before reversal and B negative before reversal, we will thus be able to find the negative and positive mobilities respectively.

Taking the case represented in fig. 3, suppose the plate A is connected electrically with a similar plate A′, whose position with respect to the Röntgen-ray bulb is so adjusted that it receives after each discharge a quantity of electricity represented graphically by the straight line ABC in the figure. Thus, considering the quantity jointly received by the plates A and A′, the relation between Q and t will be represented by the curve DOE, whose ordinates are obtained by adding those of the two curves ABC, LPM; in other words, as long as t is negative there is, on the whole, no

charge added to the plates A and A', but as soon as there is any appreciable interval between the Röntgen ray discharge and a succeeding reversal of potential on the plate B, a charge of electricity is obtained which can be detected by the ordinary electrical means, *e.g.* by connecting the two plates to an electrometer or electroscope. In this way the position of the nick at P or of the corresponding point O on the time axis can be determined. In a similar manner, in order to determine the position of the point Q, we would connect the plate A to a plate A', adjusted in such a way as to continually receive a charge represented by the straight line FGH in the figure. Thus the two plates jointly would receive a charge KST, and the position of S or Q could be readily determined by noting the time interval *t*, on one side of which we obtained a charge on the measuring instrument and on the other side of which no charge was obtained.

This null method of obtaining the positions of the nicks in the different curves was employed in most of the experiments described in this paper. In actual practice the charge given to the auxiliary plate was adjusted in such a way that on one side of the nick whose position was sought we obtained a very small constant charge (instead of no charge as in the theory), while on the other side we would obtain charges of a sign opposite to this small charge. By using this method the nicks were well defined and thus a high degree of accuracy was obtainable. In addition, it can be readily seen that the null method is independent of the intensity of the flash of Röntgen rays, whereas, if the complete curve be drawn as in the figure, the flash has to be maintained constant in intensity throughout the observations. It is worthy of mention that, under the conditions just described, the mobilities are really determined for those ions which are formed in the thin layer of gas or vapour in the vicinity of the plate A.

3. *Experimental Arrangement.*

The diagram of connections and the disposition of apparatus is given in fig. 4 ; in the main it is the same as that used by M. LANGEVIN, but certain necessary modifications were introduced to suit the special conditions.

W and W' are two iron weights which are supported by means of an electromagnet ; when the circuit through the magnet is broken, the weights fall simultaneously and break the platinum contacts at K and K' respectively. The breaking of the contact at K', which is in the primary circuit of a Marconi induction coil, gives rise to an induced E.M.F. in the secondary, and causes a momentary discharge to pass in the Röntgen-ray bulb X ; the breaking of the contact at K reverses the potential of the lower plate B of one of the chambers, as can be readily seen from the diagram, R being a water resistance of the order of 1 megohm and B at the time of breaking being at the same potential as the point β. K' can be fixed at any point of a vertical scale, thus enabling the potential of B to be reversed at any convenient interval after the passage of the discharge. This vertical scale was graduated and the

position of K′ with regard to K could thus be read off at once ; but when greater accuracy was required the position of K′ was ascertained by means of a cathetometer. C is a capacity of about 7 microfarads inserted in parallel with the primary of the induction coil in order to prevent sparking at the contact K′. When the spark was entirely eliminated it was found that, provided the current as measured by the ammeter Am was kept constant, the intensity of the Röntgen-ray flash was sensibly constant at each discharge.
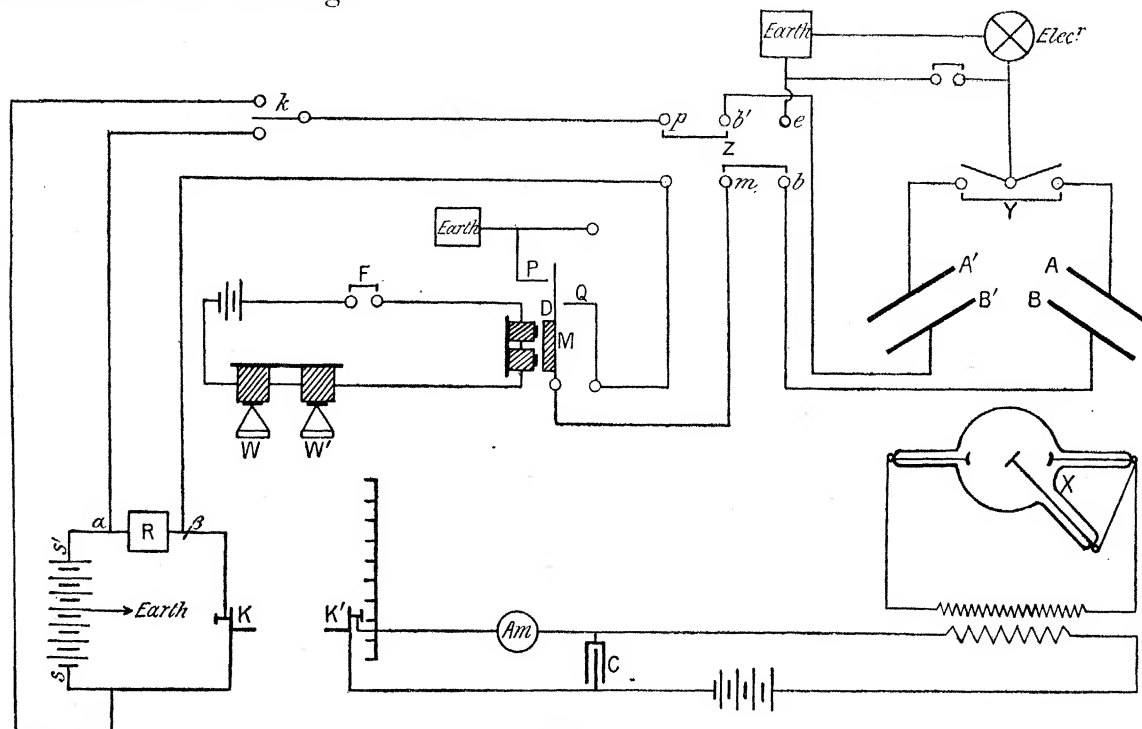

Fig. 4.

AB and A′B′ denote the ionisation chambers which are described below ; the upper electrodes A and A′ could, by means of the key Y, be connected separately to the insulated pair of quadrants of an electrometer, or could be connected together either with or without connection with the electrometer. The lower plate B′ of the chamber A′B′ is connected with the point b' of the key Z, and from the diagram it can be seen that, when b' and e are joined, B′ is permanently earthed, while, when b' and p are joined, B′ can be put permanently either at a positive or negative potential by means of the key k. The lower plate B of the chamber AB is connected with the point b of the key Z ; thus, when b and e are joined, B is permanently earthed, while, when b and m are joined, B is at the potential of the movable arm D of a magnetic relay M. When this arm is in contact with the point P, B is thus at zero potential, while, when the arm is in contact with Q, B is at the same potential as the point β, a potential which, as above described, is reversed in sign by breaking the contact at K. The object of this relay is described below under section 4.

The potentials necessary to establish the electric fields in the ionisation chambers

were obtained from a suitable number of small lead accumulators, the potential difference afforded by each being approximately 2·02 volts.

The Röntgen-ray bulb was enclosed in a lead-covered box with apertures of dimensions sufficient to allow the rays to have access to the chambers.

For a more detailed account of the essential features of the arrangement the reader is referred to LANGEVIN's original memoir.
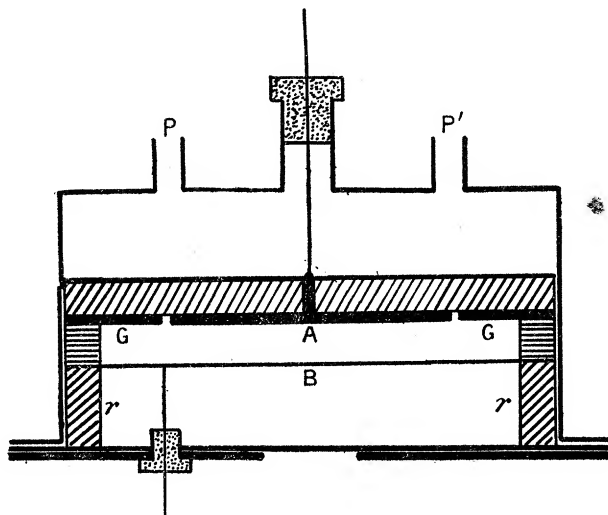

Fig. 5.

The Ionisation Chambers.—The two ionisation chambers represented by AB and A'B' in fig. 4 were exactly identical in structure and dimensions; a longitudinal section of one of them is shown in fig. 5. The upper electrode A was a brass disc of diameter 5·91 cm., and was surrounded by a brass guard-ring G, the outer diameter of which was 9 cm. A and G were screwed on to an ebonite disc, and A was connected to the electrometer by means of a wire led out through an ebonite plug. The guard-ring G and the electrode A were separated from the lower electrode B, which was of aluminium, by means of an ebonite ring perforated in several places to allow the gas or vapour to have free access to the space between the electrodes. The distance between A and B was exactly 1 cm. B was connected with the point *b* of the key Z (fig. 4) by means of a wire led out through an ebonite plug, and was kept tightly in position by means of the ebonite ring *rr*. The bottom of the chamber consisted of an aluminium disc together with an outer covering of thick lead with a central aperture of diameter 3·56 cm. The Röntgen rays passed through this aperture in the lead and through the aluminium constituting both the bottom of the vessel and the electrode B ; the gas or vapour between the electrodes was thus ionised, and in addition there was strong secondary ionisation produced in the layers of gas or vapour in the vicinity of the electrode A. The effect of the outer lead covering was to confine the ionisation to the central portion of the interval between the electrodes A and B.

P and P' are tubes soldered on to the upper brass covering of the chamber in order to afford an entrance for the gas or vapour, and also to admit of the vessel being connected to a gauge or pump. In order to keep the vessel air-tight, a rubber band, with a mixture of beeswax and resin spread uniformly over its surfaces, was inserted between the outer brass and aluminium coverings which, after being heated, were screwed tightly together.

Electrometer.—The electrometer was of the Dolezalek pattern with a platinum suspension. The needle was charged to a potential of 80 volts, which was found to be the voltage most suitable for the conditions of the experiment; with this potential, which did not however correspond to the most sensitive condition, the electrometer afforded a deflection per volt of 420 mm. on a scale about 1 metre distant. As a matter of fact, an exact determination of the sensitiveness of the electrometer was not essential in the present investigation inasmuch as it is only the sign of the charge that it is necessary to know in order to determine the points of discontinuous curvature referred to in section 2.

The leads from the upper electrodes to the electrometer quadrants were all screened by brass tubing kept at zero potential.

4. *Sources of Error.*—A. *Theoretical Assumptions.*

Duration of Röntgen - ray Discharge.—It is assumed in the theory that the duration of the discharge proceeding from the Röntgen-ray bulb is small compared with the time an ion takes to describe the distance between the electrodes. This duration has been estimated[*] to be of the order 10^{-4} second; the times measured in this experiment varied from about 0·01 to 0·03 second.

Reversal of Potential.—After the contact K has been broken, the potential of B is reversed in sign; this reversal necessarily occupies time inasmuch as B has to pass through all intermediate potentials. This time is less than the product RC, where R denotes the resistance (fig. 4) and C the capacity of the leads and electrode. This product in the present case was certainly not greater than 10^{-4} second.

Influence of the Ionisation on the Electrostatic Field.—LANGEVIN has shown that in the case of uniform ionisation, owing to the distortion of the field by the presence of free ions, the time taken by an ion to traverse any distance is increased in a ratio numerically inferior to $Q_0/12\sigma$, where Q_0 denotes the total charge of the ions of one sign and σ the charge induced on the upper plate when the potential on the lower plate is withdrawn.

For this reason it is advantageous to use, wherever possible, high voltages, but if the voltages were made too high, the time taken by the ion to cross the distance between the electrodes might become unduly small and the working error proportionately large. On this account it was difficult to obtain concordant results when

* BRUNHES, 'Comptes Rendus,' vol. 130, p. 1007, 1900.

estimating the mobilities at pressures less than 1 cm. of mercury, the workable voltages being necessarily small and the field thus being likely to be disturbed by the presence of free ions. In general, however, voltages were chosen so as to render the influence of the ionisation on the field practically negligible.

B. *Experimental Difficulties.*

Hysteresis.—When the magnet circuit is broken, both weights W and W′ should fall simultaneously; if this occur, the point P in fig. 3 should correspond to a position of K′ on the movable scale, exactly on a level with the position of K. The position of K′ corresponding to a zero time interval between the breaking of the two contacts could be accurately ascertained by the null method; in general this position of K′ occurred when at the same level as K, but after the cells which worked the magnets had been in use for a period, usually of about two weeks, it was ascertained that the weights did not continue to fall simultaneously, an effect probably due to unequal hysteresis in the two magnet cores. In such a case fresh cells were usually inserted, but the effect gradually disappeared on reversing the current through the solenoids of the magnet.

Absorption of Charge by the Insulation.—If the lower electrode B be at a fairly high potential, *e.g.* 80 volts, and then the potential be reversed, a charge will be present on the upper electrode A and its connections; if now the lower electrode be brought back to its original potential, there should on the whole be no free charge on A; with some vapours, however, it was found that a charge remained on A often quite considerable in comparison with the charges due to the ionisation of the gas when exposed to a flash of Röntgen rays. This residual charge was due to the absorption by the insulation of a part of the charge resulting from induction. To reduce this absorption to a minimum, use was made of the magnetic relay M (fig. 4). As long as the weights W, W′ remained suspended, the arm D of the relay was in contact with the point P, and so the lower electrode B was at zero potential; but when the magnet circuit was broken by the key F, the arm D came in contact with the point Q while the weights were still falling freely, and thus the electrode B was brought to the required potential. This potential was then reversed by the breaking of the contact K, and finally B was brought back to zero potential. By thus restricting the period during which B was charged to a very short duration, it was found that the effect due to the absorption by the insulation of the charge resulting from induction was negligible.

5. *Experimental Procedure.*

The two ionisation chambers were adjusted in such a way that the same flash from the Röntgen-ray bulb produced in each equal quantities of electricity of any one sign. Preliminary tests were made to ensure that the insulation was good and that there was no appreciable absorption of the charge by the insulation.

A single reading was then taken in the following manner (the null method being employed) :—

(i) K′ (fig. 4) is adjusted to the required height on the scale.

(ii) A and A′ are connected together by means of the key Y and are earthed ; the quadrants also are at zero potential. In the key Z, b and m are connected, as also are b' and p. The contact K is made.

(iii) The magnet circuit is completed at F ; the weights W and W′ are placed in position ; the movable arm D of the relay M makes contact with P, thus putting B at zero potential.

(iv) A and A′ (which throughout remain connected) are insulated ; the quadrants, however, remain earthed.

(v) The contact K′ is made ; the magnet circuit is broken at F ; the arm D makes contact with Q, thus bringing B to the required potential ; the contact K′ is broken by W′, thus giving rise to a flash of Röntgen rays which ionises the gas in each chamber ; after the desired interval the contact K is broken by W, thus reversing the potential on the electrode B.

(vi) By the time the weights have fallen, the ions will have had sufficient time to be all received at the electrodes ; the key connecting b and m (in Z) is then removed and placed so as to connect b and e, thus bringing B again to zero potential.

(vii) The quadrant pair is insulated ; the deflection due to the total charge received by A and A′ is then observed and noted.

When the potential V is established on the electrode B, the upper electrode system AA′ will be raised to a potential v proportional to V. The value of v corresponding to any definite potential V was determined experimentally in the following manner. The upper electrode system was connected to the electrometer and the steady deflection d was noted when B was raised to the potential V. The quadrants were then earthed and the upper electrode system was charged to a known small potential v' by means of a potentiometer ; the system was then disconnected from the potentiometer and connected to the insulated uncharged quadrant pair, causing a steady deflection d'. The potential v' was then varied until d' became equal to d ; this value of v' corresponds to the required potential v. As a result of a series of observations with different values of V, it was deduced that when the electrode B was raised from zero potential to a potential of V volts, the upper electrode system attained a potential of 0.0425 V volt.[*]

The corresponding electric field, which was sensibly uniform in the region to which the ionisation was confined, was thus 0.9575 V volt per centimetre.

* The potential v should also be given by $d^2/d_1\delta$, where d denotes the steady deflection as above, d_1 denotes the steady deflection resulting from reconnecting the upper electrode system to the quadrants after they have been earthed and insulated, and δ denotes the sensitiveness of the electrometer over the range of deflections under consideration. A series of observations led to the same result as above.

The actual potentials of B and B′ during the experiment will, of course, depend, as above explained (section 2), on the particular nick in the curve whose position is sought ; these potentials are controlled by means of the key k, and also by adjustable connections (s and s') at the battery.
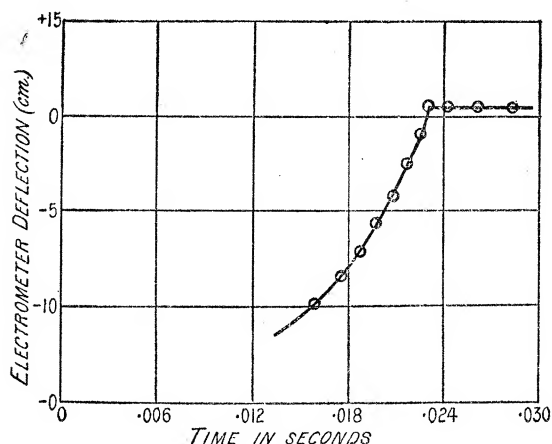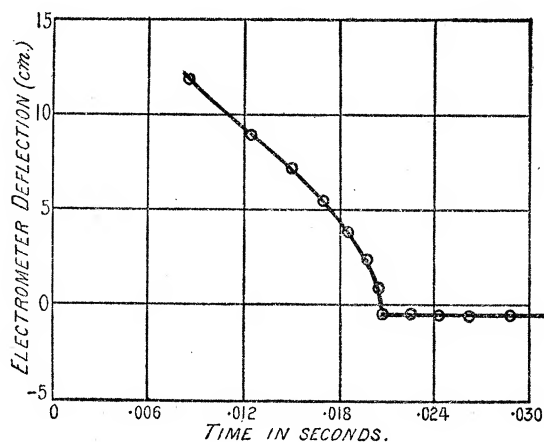

Fig. 6.

Fig. 7.

In fig. 6 and fig. 7 are given typical curves which were obtained by the null method from observations made to determine the position of the nicks corresponding to the negative and positive velocities respectively in sulphur dioxide at a pressure of 269 mm. of mercury, the electric field being 38·7 volts per centimetre.

6. *Manipulation of Gases and Vapours.*

The *atmospheric air* employed was dried by passing through phosphorus pentoxide.

The *nitrous oxide* and *carbon dioxide* were obtained from cylinders of compressed gas and were dried by passing through phosphorus pentoxide.

The *ammonia* was obtained from a cylinder of the compressed gas and was dried by passing through solid potassium hydroxide.

The *carbon monoxide* was liberated by the action of sulphuric acid on sodium formate and was dried by passing through phosphorus pentoxide.

The *sulphur dioxide* was liberated by the action of dilute sulphuric acid on sodium sulphite and was dried by passing through calcium chloride.

The vapours employed were, in most cases, dried according to the method followed by W. H. PERKIN* in his investigation of the "Magnetic Rotary Polarisation of Compounds in relation to their Chemical Constitution." In all cases Kahlbaum's preparations were used.

The *ethyl alcohol, methyl acetate, ethyl formate,* and *ethyl acetate* were from samples kindly lent me by Mr. T. H. LABY, who had previously obtained them by fractionating and drying Kahlbaum's preparations till each sample had a constant boiling-point.

* 'Journ. Chem. Soc. Trans.,' vol. 45, p. 421, 1884.

In addition to the ethyl ether obtained from Kahlbaum ether from another source was fractionally distilled three times, the last time with metallic sodium, and the portion boiling at 35°·2 C. (barometer 769 mm.) was collected and used. The resulting mobilities were in concordance with those previously obtained.

The ionisation chambers were exhausted by means of a Töpler mercury pump; in the case of a gas it was admitted to the pump and the pressure could be diminished or increased with comparative ease; in the case of a vapour the pump was first of all disconnected by means of a tap and the liquid allowed to evaporate into the apparatus till the requisite pressure was obtained. Often a stream of vapour was passed through by means of a water pump, thus ensuring that any air which had remained in the apparatus was removed.

As is usually the case when working with vapours, the pressure at first decreases owing to partial condensation; it, however, ultimately reaches a steady state. It is possible, moreover, that some chemical action between the vapour and the metal of the ionisation chambers might interfere with the mobility values; the best way of investigating this point is to find the ionic mobilities in the vapour under conditions as varied as possible. In certain instances the values obtained were not concordant; these values are given in the table of results, but are not used in calculating the mean mobilities. In general, however, the values obtained over widely different conditions were in good agreement.

The pressures were measured by means of a mercury gauge, one limb of which had been previously exhausted to a high vacuum by means of the Töpler pump and then sealed; in this manner the pressure readings were made independent of the barometric reading.

7. *Experimental Results.*

In estimating the ionic mobilities in a gas or vapour, it is important to secure as wide a variation as possible in the experimental conditions; such a variation was obtained in the following ways :—

(i) The mobilities were estimated in different samples of the gas or vapour.

(ii) The mobilities were often measured in each of the two ionisation chambers, the remaining one in each case serving as the standard.

(iii) The electric field was made to vary over as wide a range as was practicable.

(iv) The mobilities were measured over a wide range of pressures.

(v) The experiments were often repeated after a lapse of several weeks, other gases or vapours having in the meantime been experimented upon.

Under conditions so varied it was only to be expected that variations should occur in the mobility values; most of the variations were within 7 per cent. of the mean value. The actual experimental conditions and the results obtained are exhibited in the following tables; the values apply to a mean temperature of about 15° C., but it

will be noticed that, although the actual temperatures are given, no correction has been made, as such correction would almost certainly lie within the limits of error of the experiment.

The figures in the second column give the electric field X in volts per centimetre. The third and fourth columns give the height in centimetres from the bottom of the falling weight W′ to the movable contact K′, when the latter is in the positions corresponding respectively to the first and second nicks in the typical curve (*vide* fig. 3, which was obtained in the measurement of a negative mobility). The fifth column contains the equivalent time interval t expressed as the fraction of a second; it was calculated by means of the ordinary formula for a body falling freely under gravity. The values in centimetres per second of the mobility k are calculated from the equation $k = 1/Xt$, and, corresponding to the stated pressure, are given in the seventh column. In the eighth and ninth columns are given the mobilities corresponding to a potential gradient of 1 volt per centimetre and to a pressure of 760 mm. of mercury; these values are based on the assumption that the ionic velocity is proportional to the field intensity and is inversely proportional to the pressure.

An asterisk affixed to a mobility value denotes that this value was not included in estimating the mean; these values showed marked deviations from the law $pk = $ constant, the reasons for these deviations in some cases not being apparent, but in most cases being due to the pressures lying outside the range for which the law is applicable.

Tem-perature.	Electric field.	Height of fall to		Time.	Pressure.	k	k_{760}.	
		1st point.	2nd point.				+	−
° C.	volts/cm.	cm.	cm.	sec.	mm.	cm./sec.	cm./sec.	cm./sec.
					AIR.			
14	38·7	54·8	50·0	0·0150	758	1·72		1·7
			49·5	0·0166	758	1·56	1·55	
16·5			50·0	0·0150	762	1·72		1·73
			49·5	0·0166	762	1·56	1·56	
			52·5	0·0071	380	3·64		1·82
			52·1	0·0083	380	3·11	1·56	
			50·3	0·0140	760	1·85		1·85
			49·5	0·0166	760	1·56	1·56	
	15·5		50·7	0·0127	264	5·08		1·76
			50·0	0·0150	264	4·30	1·49	
	5·8		51·0	0·0118	98	14·61		1·88*
			50·0	0·0150	102	11·59	1·54*	

Mean values of k_{760} $\begin{cases} \text{positive ion} & 1·54 \text{ cm./sec.} \\ \text{negative ,,} & 1·78 \quad ,, \end{cases}$

Temperature.	Electric field.	Height of fall to		Time.	Pressure.	k.	k_{760}.	
		1st point.	2nd point.				+	−
°C.	volts/cm.	cm.	cm.	sec.	mm.	cm./sec.	cm./sec.	cm./sec.

CARBON MONOXIDE.

14	38·7	54·8	51·3	0·0108	355	2·39	1·12	
	19·3		48·5	0·0198	347	2·62		1·19
			51·2	0·0112	173	4·63		1·05
13	38·7		47·8	0·0221	759	1·17		1·17
			51·2	0·0112	361	2·31	1·09	
			51·5	0·0102	361	2·53		1·20
	19·3		50·7	0·0127	201	4·08	1·08	
			50·9	0·0121	201	4·28		1·13
	7·7		50·4	0·0137	93	9·48	1·16	
			50·4	0·0137	93	9·48		1·16
	3·9		51·5	0·0102	34	25·13		1·12
			51·0	0·0118	36	21·72	1·03	

Mean values of k_{760} $\begin{cases} \text{positive ion } 1\cdot10 \text{ cm./sec.} \\ \text{negative ,, } 1\cdot14 \text{ ,,} \end{cases}$

CARBON DIOXIDE.

15	77·4	55·0	50·2	0·0149	754	0·87		0·86
			50·0	0·0156	754	0·83	0·82	
	38·7	54·8	52·2	0·0080	200	3·23		0·85
			52·1	0·0083	200	3·11	0·82	
	77·4		49·8	0·0156	760	0·83		0·83
			49·5	0·0166	760	0·78	0·78	
	17·4		53·2	0·0049	60	11·73		0·93*
			53·0	0·0055	60	10·45	0·82*	

Mean values of k_{760} $\begin{cases} \text{positive ion } 0\cdot81 \text{ cm./sec.} \\ \text{negative ,, } 0\cdot85 \text{ ,,} \end{cases}$

NITROUS OXIDE.

15	77·4	55·0	50·4	0·0143	754	0·90		0·90
			50·2	0·0149	754	0·87	0·86	
			50·3	0·0146	766	0·88		0·89
			50·0	0·0156	766	0·83	0·83	
			50·4	0·0143	762	0·90		0·91
16	19·3		49·3	0·0178	241	2·91		0·92
			48·5	0·0204	241	2·54	0·81	
	5·8		51·0	0·0124	51	13·91		0·93*
			50·7	0·0134	51	12·87	0·86*	
17	38·7	54·8	45·5	0·0297	791	0·87		0·91
			49·7	0·0159	419	1·62		0·90
	19·3		50·8	0·0124	167	4·18		0·92
	38·7		46·0	0·0280	741	0·92		0·90
			45·0	0·0314	741	0·82	0·80	
	15·5		45·5	0·0297	307	2·17		0·88
			44·8	0·0320	307	2·02	0·81	
	1·9		50·0	0·0150	23	35·08		1·06*
			49·5	0·0166	23	31·70	0·96*	

Mean values of k_{760} $\begin{cases} \text{positive ion } 0\cdot82 \text{ cm./sec.} \\ \text{negative ,, } 0\cdot90 \text{ ,,} \end{cases}$

Tem-perature.	Electric field.	Height of fall to		Time.	Pressure.	k.	k_{760}.	
		1st point.	2nd point.				+	−
° C.	volts/cm.	cm.	cm.	sec.	mm.	cm./sec.	cm./sec.	cm./sec.

AMMONIA.

13	77·4	54·9	50·8	0·0127	602	1·02		0·81
			50·5	0·0136	590	0·95	0·74	
14	38·7	54·8	49·6	0·0162	348	1·59	0·73	
			50·0	0·0150	348	1·72		0·79
	77·4		52·4	0·0074	350	1·75		0·80
	38·7		50·7	0·0127	294	2·03		0·79
			50·3	0·0140	296	1·85	0·72	
	19·3		50·3	0·0140	162	3·70		0·79
			50·0	0·0150	162	3·45	0·74	
	38·7		49·3	0·0172	408	1·50		0·81
			49·2	0·0175	387	1·48	0·75	

Mean values of k_{760} $\begin{cases} \text{positive ion } 0·74 \text{ cm./sec.} \\ \text{negative ,, } 0·80 \text{ ,,} \end{cases}$

ALDEHYDE.

13	38·7	54·8	49·7	0·0159	145	1·62		0·31
			50·1	0·0146	137	1·77	0·32	
			50·7	0·0127	109	2·03	0·29	
			50·6	0·0131	107	1·97		0·28
	19·3		47·2	0·0240	107	2·16		0·30
			47·7	0·0224	103	2·31	0·31	
			50·4	0·0137	57	3·78		0·28
			50·8	0·0124	57	4·18	0·31	
15	38·7		46·7	0·0257	223	1·01	0·29	
			46·7	0·0257	219	1·01		0·30
13			46·6	0·0260	240	0·99		0·31
			47·0	0·0247	238	1·05	0·33	
			49·3	0·0172	164	1·50	0·32	
			49·0	0·0182	164	1·42		0·31
	19·3		49·3	0·0172	78	3·01	0·31	
			49·1	0·0179	78	2·89		0·30

Mean values of k_{760} $\begin{cases} \text{positive ion } 0·31 \text{ cm./sec.} \\ \text{negative ,, } 0·30 \text{ ,,} \end{cases}$

ETHYL ALCOHOL.

16	9·7	54·8	51·2	0·0112	24	9·20		0·29
			51·7	0·0096	24	10·74	0·34	
	7·7		50·6	0·0131	26	9·91	0·34	
			49·3	0·0172	26	7·55		0·26
			50·6	0·0131	26	9·91	0·34	
			49·3	0·0172	26	7·55		0·26
	9·7		50·8	0·0124	26	8·31		0·28
			51·5	0·0102	26	10·11	0·35	

Mean values of k_{760} $\begin{cases} \text{positive ion } 0·34 \text{ cm./sec.} \\ \text{negative ,, } 0·27 \text{ ,,} \end{cases}$

Temperature.	Electric field.	Height of fall to		Time.	Pressure.	k.	k_{760}.	
		1st point.	2nd point.				+	−
° C.	volts/cm.	cm.	cm.	sec.	mm.	cm./sec.	cm./sec.	cm./sec.

ACETON.

Temperature.	Electric field.	1st point.	2nd point.	Time.	Pressure.	k.	+	−
14	15·5	55·0	48·7	0·0198	69	3·26		0·30
			49·3	0·0178	69	3·62	0·33	
			49·2	0·0181	65	3·56	0·30	
	38·7		52·6	0·0074	65	3·49		0·30
	19·3	54·8	51·0	0·0118	56	4·39	0·32	
	.		50·3	0·0140	58	3·70		0·28
			49·0	0·0182	84	2·85	0·31	
	13·5		49·3	0·0172	52	4·32		0·29
	38·7		50·8	0·0124	106	2·08		0·29
			51·3	0·0108	106	2·39	0·33	
	19·3		49·4	0·0169	78	3·07	0·31	
20			48·7	0·0191	82	2·71	0·29	
			48·5	0·0198	82	2·62		0·28
	15·5		50·0	0·0150	54	4·30		0·31
	9·7		49·5	0·0166	35	6·21		0·29
			50·0	0·0150	35	6·87	0·32	
	19·3		50·2	0·0143	73	3·62		0·35*
			50·6	0·0131	73	3·95	0·38*	

Mean values of k_{760} $\begin{cases} \text{positive ion} & 0·31 \text{ cm./sec.} \\ \text{negative ,,} & 0·29 \quad ,, \end{cases}$

SULPHUR DIOXIDE.

Temperature.	Electric field.	1st point.	2nd point.	Time.	Pressure.	k.	+	−
18·5	77·4	54·8	48·4	0·0201	487	0·64		0·41
			49·0	0·0182	483	0·71	0·45	
			48·7	0·0191	459	0·68		0·41
			49·0	0·0182	457	0·71	0·43	
	38·7		48·2	0·0208	269	1·24	0·44	
			47·5	0·0230	269	1·12		0·40
	19·3		46·0	0·0280	170	1·85		0·41
			46·6	0·0260	170	1·99	0·45	
	116·0		50·6	0·0131	496	0·66		0·43
			50·8	0·0124	489	0·69	0·45	
	77·4		49·0	0·0182	464	0·71	0·43	
			48·7	0·0191	454	0·68		0·40
	38·7		48·0	0·0214	247	1·20		0·39
			48·5	0·0198	247	1·30	0·42	
19	154·7		49·9	0·0153	711	0·42		0·39
			50·3	0·0140	711	0·46	0·43	
	15·5	55·0	49·9	0·0158	79	4·08		0·42
			50·4	0·0143	79	4·51	0·47	

Mean values of k_{760} $\begin{cases} \text{positive ion} & 0·44 \text{ cm./sec.} \\ \text{negative ,,} & 0·41 \quad ,, \end{cases}$

Tem-perature.	Electric field.	Height of fall to		Time.	Pressure.	k.	k_{760}.	
		1st point.	2nd point.				+	−
° C.	volts/cm.	cm.	cm.	sec.	mm.	cm./sec.	cm./sec.	cm./sec.

ETHYL CHLORIDE.

Table I.

14	77·4	54·8	46·7	0·0257	419	0·50	0·28	
			46·9	0·0250	407	0·52		0·28
13			47·0	0·0247	374	0·52		0·26
			47·3	0·0237	364	0·54	0·26	
15			48·2	0·0208	338	0·62		0·28
			48·3	0·0204	333	0·63		0·28
			48·9	0·0185	324	0·70	0·30	
			48·7	0·0191	316	0·68		0·28
13			49·8	0·0156	256	0·83	0·28	
			50·6	0·0131	221	0·99		0·29
			50·7	0·0127	220	1·02	0·29	
14	38·7		47·4	0·0234	205	1·10	0·30	
	77·4		51·1	0·0115	203	1·12	0·30	

Mean values of k_{760} $\begin{cases} \text{positive ion } 0·29 \text{ cm./sec.} \\ \text{negative } \,,, \;\; 0·28 \quad \,,, \end{cases}$

Table II.

15	77·4	54·8	50·5	0·0134	232	0·96		0·29
			50·9	0·0121	230	1·07	0·32	
13			51·4	0·0105	201	1·23		0·33
			51·6	0·0099	199	1·31	0·34	
			51·5	0·0102	196	1·27	0·33	
			51·5	0·0102	193	1·37		0·32
	38·7		48·1	0·0211	186	1·22		0·30
			51·4	0·0105	103	2·46	0·33	
			51·8	0·0093	91	2·78	0·33	
			51·9	0·0090	83	2·87		0·31
	5·8		46·6	0·0260	36	6·63		0·31
			50·0	0·0150	22	11·50	0·33	
	7·7		50·9	0·0121	22	10·73		0·31
	3·9		49·9	0·0153	16	16·76	0·35	
			49·5	0·0166	16	15·44		0·32
	5·8		51·2	0·0112	16	15·40		0·32
			51·7	0·0096	15	17·96	0·35	

Mean values of k_{760} $\begin{cases} \text{positive ion } 0·33 \text{ cm./sec.} \\ \text{negative } \,,, \;\; 0·31 \quad \,,, \end{cases}$

The explanation of this double tabulation of values is given later under section 8.

Temperature.	Electric field.	Height of fall to		Time.	Pressure.	k.	k_{760}.	
		1st point.	2nd point.				+	−
° C.	volts/cm.	cm.	cm.	sec.	mm.	cm./sec.	cm./sec.	cm./sec.

PENTANE.

Temperature.	Electric field.	1st point.	2nd point.	Time.	Pressure.	k.	+	−
14	38·7	54·8	48·0	0·0214	217	1·21	0·34	
			48·2	0·0208	215	1·24	0·35	
			49·4	0·0169	171	1·53		0·34
			49·3	0·0172	173	1·50	0·34	
			49·3	0·0172	173	1·50		0·34
	19·3		50·8	0·0124	67	4·18	0·37	
			50·8	0·0124	67	4·18		0·37
13	38·7		47·5	0·0230	228	1·12		0·34
			48·0	0·0214	222	1·21	0·35	
			48·2	0·0208	222	1·24		0·36
			48·4	0·0201	218	1·28	0·37	
			48·2	0·0208	216	1·24		0·35
	77·4		49·5	0·0166	370	0·78	0·38	
			49·5	0·0166	366	0·78		0·37
14	38·7		50·8	0·0124	128	2·08		0·35
			50·8	0·0124	128	2·08	0·35	
	77·4		50·3	0·0140	302	0·92		0·37
			50·3	0·0140	302	0·92	0·37	

Mean values of k_{760} $\begin{cases} \text{positive ion } 0·36 \text{ cm./sec.} \\ \text{negative } \text{,,} \quad 0·35 \quad \text{,,} \end{cases}$

METHYL ACETATE.

Temperature.	Electric field.	1st point.	2nd point.	Time.	Pressure.	k.	+	−
19·5	19·3	54·8	49·8	0·0156	86	3·32		0·38
			49·7	0·0159	84	3·26	0·36	
	38·7		51·3	0·0108	100	2·39	0·31	
			51·6	0·0099	99	2·61		0·34
	19·3		49·6	0·0162	80	3·20		0·34
			49·4	0·0169	78	3·07	0·31	
20·5	15·5	55·0	49·5	0·0172	70	3·75	0·34	
			49·8	0·0162	71	3·98		0·37

Mean values of k_{760} $\begin{cases} \text{positive ion } 0·33 \text{ cm./sec.} \\ \text{negative } \text{,,} \quad 0·36 \quad \text{,,} \end{cases}$

ETHYL FORMATE.

Temperature.	Electric field.	1st point.	2nd point.	Time.	Pressure.	k.	+	−
20·5	19·3	54·8	48·9	0·0185	87	2·80	0·32	
			48·9	0·0185	87	2·80		0·32
	38·7		50·9	0·0121	114	2·13		0·32
	19·3	55·0	48·4	0·0207	93	2·50		0·31
			48·8	0·0194	83	2·87	0·29	
			49·3	0·0178	83	2·91		0·32
		54·8	48·0	0·0214	93	2·42		0·30
	38·7		51·4	0·0105	91	2·46		0·29
			51·4	0·0105	91	2·46	0·29	
	19·3		48·5	0·0198	89	2·62	0·31	
			48·5	0·0198	89	2·62		0·31

Mean values of k_{760} $\begin{cases} \text{positive ion } 0·30 \text{ cm./sec.} \\ \text{negative } \text{,,} \quad 0·31 \quad \text{,,} \end{cases}$

Temperature.	Electric field.	Height of fall to		Time.	Pressure.	k.	k_{760}.	
		1st point.	2nd point.				+	−
° C.	volts/cm.	cm.	cm.	sec.	mm.	cm./sec.	cm./sec.	cm./sec.

ETHYL ETHER.

9	38·7	54·8	49·5	0·0166	154	1·56		0·32
			49·2	0·0175	154	1·48	0·30	
			50·6	0·0131	110	1·97	0·29	
			50·7	0·0127	114	2·03		0·30
10			48·5	0·0198	176	1·30		0·30
			51·3	0·0108	94	2·39		0·30
		54·9	48·0	0·0217	200	1·19		0·31
			47·6	0·0230	198	1·12	0·29	
			46·5	0·0267	234	0·97		0·30
19		54·8	48·9	0·0185	159	1·40		0·29
			48·9	0·0185	155	1·40	0·28	
	13·5		49·5	0·0166	58	4·46		0·34
	7·7		49·0	0·0182	32	7·13		0·30
18·5	38·7		50·3	0·0140	137	1·85		0·33
			49·2	0·0175	176	1·48		0·34
			49·2	0·0175	157	1·48	0·30	
9			46·6	0·0260	204	0·99		0·27*
			46·6	0·0260	198	0·99	0·26*	

Mean values of k_{760} { positive ion 0·29 cm./sec. / negative „ 0·31 „

ETHYL ACETATE.

19	9·7	54·8	50·3	0·0140	28	7·36		0·27
			50·9	0·0121	28	8·52	0·31	
	5·8		48·2	0·0208	28	8·29	0·30	
			47·9	0·0217	28	7·94		0·29
	19·3		51·2	0·0112	46	4·63		0·28
			51·5	·0·0102	46	5·08	0·31	

Mean values of k_{760} { positive ion 0·31 cm./sec. / negative „ 0·28 „

METHYL BROMIDE.

22	77·4	55·0	46·5	0·0270	404	0·48		0·25
			47·5	0·0237	384	0·54	0·27	
			49·3	0·0178	296	0·73	0·28	
			49·2	0·0181	298	0·71		0·28
	38·7		50·5	0·0139	125	1·86		0·31
			50·6	0·0136	125	1·90	0·31	
	19·3		51·0	0·0124	57	4·18	0·31	
			50·7	0·0134	59	3·86		0·30
	13·5		50·3	0·0146	42	5·07		0·28
			50·7	0·0134	42	5·53	0·30	

Mean values of k_{760} { positive ion 0·29 cm./sec. / negative „ 0·28 „

Temperature.	Electric field.	Height of fall to		Time.	Pressure.	k.	k_{760}.	
		1st point.	2nd point.				+	−
° C.	volts/cm.	cm.	cm.	sec.	mm.	cm./sec.	cm./sec.	cm./sec.

METHYL IODIDE.

Temperature.	Electric field.	1st point.	2nd point.	Time.	Pressure.	k.	+	−
10	38·7	54·9	47·0	0·0250	178	1·03		0·24
	77·4		50·2	0·0146	182	0·88	0·21	
	38·7		51·2	0·0114	74	2·27		0·22
			50·9	0·0124	74	2·08	0·20	
			47·3	0·0240	138	1·08		0·20
	19·3	54·8	53·0	0·0055	18	9·42		0·22
			53·3	0·0046	14	11·26	0·21	
	38·7		51·6	0·0099	64	2·61		0·22
			51·4	0·0105	64	2·46	0·21	

Mean values of k_{760} { positive ion 0·21 cm./sec. / negative „ 0·22 „

CARBON TETRACHLORIDE.

Temperature.	Electric field.	1st point.	2nd point.	Time.	Pressure.	k.	+	−
11	13·5	54·8	50·5	0·0134	43	5·53		0·31
			50·5	0·0134	43	5·53	0·31	
			49·8	0·0156	39	4·75	0·24	
			50·0	0·0150	39	4·94		·0·25
	9·7	55·0	50·6	0·0136	34	7·58		0·34
	15·5		50·3	0·0146	56	4·42		0·33
			50·3	0·0146	59	4·42	0·34	
			50·3	0·0146	59	4·42		0·34
20	9·7		50·6	0·0136	32	7·58	0·32	
	15·5		50·9	0·0128	48	5·04		0·32
			50·7	0·0134	48	4·82	0·30	

Mean values of k_{760} { positive ion 0·30 cm./sec. / negative „ 0·31 „

ETHYL IODIDE.

Temperature.	Electric field.	1st point.	2nd point.	Time.	Pressure.	k.	+	−
10	38·7	54·9	52·4	0·0077	31	3·36		0·14
			52·7	0·0068	31	3·80	0·15	
	19·3	54·7	49·8	0·0153	37	3·39	0·16	
			49·3	0·0169	37	3·06		0·15
16		54·8	49·8	0·0156	41	3·32	0·18	
			49·6	0·0162	41	3·18		0·17
			48·3	0·0204	53	2·54	0·18	
			48·1	0·0211	53	2·45		0·17
10		54·9	49·8	0·0159	31	3·26	0·13*	
			48·8	0·0191	29	2·71		0·10*

Mean values of k_{760} { positive ion 0·17 cm./sec. / negative „ 0·16 „

In the following table is given a summary of the results obtained for the ionic mobilities; they correspond to an electric intensity of 1 volt per cm. and a pressure of 760 mm. of mercury. There is appended a table containing the values of the mobilities previously ascertained.

TABLE I.—Summary of Ionic Mobilities.

Gas or vapour.	Formula.	Molecular weight.	Absolute critical temperature.	$k_{760}.$ +	$k_{760}.$ −
			°C.	cm./sec.	cm./sec.
Air	—	—	—	1·54	1·78
Carbon monoxide	CO	28	137	1·10	1·14
Carbon dioxide	CO_2	44	304	0·81	0·85
Nitrous oxide	N_2O	44	310	0·82	0·90
Ammonia	NH_3	17	404	0·74	0·80
Aldehyde	C_2H_4O	44	454	0·31	0·30
Ethyl alcohol	C_2H_6O	46	513	0·34	0·27
Aceton	C_3H_6O	58	511	0·31	0·29
Sulphur dioxide	SO_2	64	429	0·44	0·41
Ethyl chloride	C_2H_5Cl	64·5	458	0·33	0·31
Pentane	C_5H_{12}	72	470	0·36	0·35
Methyl acetate	$C_3H_6O_2$	74	507	0·33	0·36
Ethyl formate	$C_3H_6O_2$	74	507	0·30	0·31
Ethyl ether	$C_4H_{10}O$	74	467	0·29	0·31
Ethyl acetate	$C_4H_8O_2$	88	522	0·31	0·28
Methyl bromide	CH_3Br	95	467	0·29	0·28
Methyl iodide	CH_3I	142	528	0·21	0·22
Carbon tetrachloride	CCl_4	154	557	0·30	0·31
Ethyl iodide	C_2H_5I	156	554	0·17	0·16

TABLE II.—Mobilities Previously Ascertained.

Gas.	Formula.	Molecular weight.	Absolute critical temperature.	$k_{760}.$ +	$k_{760}.$ −	Authority.
			°C.	cm./sec.	cm./sec.	
Air	—	—	—	1·36	1·87	ZELENY.
,,	—	—	—	1·60	1·70	LANGEVIN.
,,	—	—	—	1·39	1·78	PHILLIPS.
Hydrogen	H_2	2	35	6·70	7·95	ZELENY.
Helium	He	4	4·5	5·09	6·31	FRANCK and POHL.
Nitrogen	N_2	28	124	1·6*		RUTHERFORD.
Oxygen	O_2	32	154	1·36	1·80	ZELENY.
Hydrochloric acid	HCl	36·5	325	1·27*		RUTHERFORD.
Carbon dioxide	CO_2	44	304	0·76	0·81	ZELENY.
,, ,,	,,	—	—	0·86	0·90	LANGEVIN.
Sulphur ,,	SO_2	64	429	0·5*		RUTHERFORD.
Chlorine	Cl_2	71	414	1·0*		RUTHERFORD.

* Mean values.

8. *Discussion of Results.*

A first deduction from the experimental results is that for a given electric intensity the velocity of an ion varies inversely as the pressure; while, for a constant pressure, the velocity is directly proportional to the electric intensity.

LANGEVIN found that in air over a range of pressures varying from 7·5 cm. to 143 cm. of mercury the product of the pressure and the mobility of the positive ion was sensibly constant; but, in the case of the negative ion, this product showed a marked increase in value when the pressure was reduced below 20 cm.; this result was interpreted as denoting a simplification in the structure of the negative ion at relatively low pressures. The values of the mobilities given for CO_2 and N_2O in the tables show an increase in the product pk at low pressures both for the positive and negative ions. As pointed out before, the experimental error tends to increase when the mobilities are measured at low pressures; on this account no attempt was made to obtain measurements at pressures below 1 cm. of mercury.

In the case of vapours the pressures were in general chosen so that the vapour under consideration was well removed from its condensation point; under these circumstances no tendency of the product pk to increase with diminution of pressure was observed. However, attempts were made to observe whether there was any deviation from the law pk = constant as the vapour approached the saturated state; great difficulty was incurred on account of the tendency of the vapour to condense on the insulation, nevertheless, in the case of ethyl chloride, the product pk showed a marked decrease in value both for the positive and negative ions as the pressures were increased beyond 200 mm.[*] It is known from experiments on saturated vapours[†] that the density of a vapour increases more rapidly than would be expected from BOYLE's law as the vapour approaches saturation, in other words, there is a tendency for the vapour molecules to form aggregations; this would result in a diminution of the value of the product pk, either in consequence of an increased complexity of the ionic structure, or of an increased collision frequency between the ion and the molecules of the vapour. Another explanation of the alteration in value of pk is given below, under section 9; on this view the alteration depends not so much on the increase of density as on the marked increase in viscosity which has been shown[‡] to occur when a vapour approaches the saturated state.

PRZIBRAM[§] has recently measured the ionic mobilities in several vapours at a pressure of 1 atmosphere, the temperatures being chosen so as to just suffice to prevent condensation; the vapours were ionised by the α rays from polonium, and a

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[*] The vapour pressure of ethyl chloride at 10° C. is 691 mm.

[†] *Cf.* MEYER, 'Kinetic Theory of Gases,' 2nd edition, chapter 4.

[‡] *Cf.* MEYER, *loc. cit.*, chapter 7.

[§] 'Wien. Berichte,' IIa, Bd. 117, p. 665, 1908.

blast method was employed in the measurement of the mobilities.   The following results are given in PRZIBRAM's paper :—

Vapour.	$k+$.	$k-$.	Temperature.
	cm./sec.	cm./sec.	° C.
Water	0·77	0·73	100
Methyl alcohol	0·29	0·30	66
Ethyl alcohol	0·26	0·27	79
Benzol	0·18	0·21	80
Aceton	0·11	0·12	57
Chloroform.	0·19	0·16	58
Hexane	0·15	0·16	69
Ethyl ether	0·15	0·16	35
Methyl acetate	0·14	0·18	58

In the cases of ethyl alcohol, aceton, ethyl ether, and methyl acetate, it is noticeable that the mobilities are much smaller than when measured at pressures well removed from the saturated state and reduced to a pressure of 760 mm. of mercury in accordance with the law pk = constant.   It is probable that in the case of every vapour, just as has been shown in the particular case of ethyl chloride, the values of pk would decrease if pressures were chosen so as to make the vapour approach saturation.   As an analogous illustration of this point, it is worthy of mention that PHILLIPS[*] has shown that the ionic mobilities when measured in air at atmospheric pressure vary as the absolute temperature over a wide range of temperatures ; but, in the neighbourhood of the temperature of boiling liquid air, the mobilities are distinctly smaller than would be the case if this law of variation were applicable.

A preliminary examination of the results which are given in Tables I. and II. shows that there is no direct dependence of the ionic mobility on the molecular weight ; it might have been expected that the mobilities would decrease as the molecular weight increased, but that this is not always true is seen by comparing the cases of ammonia (molecular weight 17 and mean ionic mobility ·77 cm./sec.) and oxygen (molecular weight 32 and mean mobility 1·58 cm./sec.).   A better way of considering the results would be to divide the list into two groups, placing in one group those gases which have a relatively small critical temperature, and in the other those (the so-called vapours) which have a relatively high critical temperature ; it will then be seen that the high mobilities belong without exception to the gases of the first group ; the apparently small values of the ionic mobilities in certain cases, e.g. ammonia and aldehyde, can then be conceived as being due to large cohesive forces between their molecules evinced by their relatively high critical temperatures.   An attempt to deduce the mobility values from purely theoretical considerations is given later under section 9.

It is noticeable also from an inspection of the tables that, especially in the case of

* 'Roy. Soc. Proc.,' A, vol. 78, p. 167, 1906.

vapours, there is little difference in value between the positive and negative mobilities. The greatest differences are found for the elementary gases :—air, oxygen, hydrogen, and helium. There are several instances, including most of the ethyl compounds, in which the positive ion has a greater mobility than the negative; hitherto, only one gas, viz., acetylene,* was known in which this was the case.

9. *Theoretical Considerations.*

The Law of Mobility of the Ions formed in Gaseous Media.—In the following treatment, which is based on the kinetic theory of gases, an attempt is made to obtain a theoretical expression for the velocity with which a charged body of dimensions comparable with those of a molecule would move in the gas under the action of an electric field of given intensity. It is necessary at the outset to fix our ideas of a molecule and an ion; for this purpose the following conceptions are introduced :—

A *molecule* is regarded as a nucleus surrounded by a sphere of force of radius $\frac{1}{2}s$. The spheres of force are supposed mutually impenetrable.

An *ion* is regarded as involving two distinct elements :—

(i) A mass (independent of the charge). Considering this element alone, let us represent the ion as a nucleus surrounded by a sphere of force of radius $\frac{1}{2}s'$.

(ii) A charge e (electrostatic units). During motion of the ion through the gas the effect of this charge is equivalent (as will be shown) to an increase in the volume of the force sphere (i) of the ion, the mass remaining unaltered.

A *collision* occurs between two molecules when the distance between their centres is equal to the sum of the radii of their force spheres.

LANGEVIN† has shown that the velocity of an ion under unit electrostatic intensity is given by

$$k = e\mathrm{L}/\mathrm{MV},$$

where M denotes the mass of the ion, L its mean free path through the gas, and V its mean velocity of thermal agitation. As the ion moves through the gas the charge associated with it attracts the neutral molecules; there results an increase in the mean collision frequency of the ion and consequently a diminution in its mean free path.

Expression for the Mean Free Path of the Ion.—Consider the motion of an ion and a molecule regarded in the light of two interacting free particles. Let R denote the potential due to the polarisation of the molecule by the charge on the ion,‡ so that the

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* ZELENY, ' Phil. Mag.,' vol. 46, p. 132, 1898.

† ' Ann. de Chim. et de Phys.,' vii., 28, p. 335, 1903.

‡ The polarisation of the molecule by the electric field is regarded as negligible in comparison with that due to the ionic charge.

force, taken as wholly radial, between the ion and the molecule is given by $d\text{R}/dr$ at a distance r.   Let us reduce the molecule to rest and consider the relative motion as the ion approaches it so that the velocity at infinity was U.   The interacting forces must now be considered as being derived from a potential $\dfrac{\text{M}+m}{m}$ R, m denoting the mass of the molecule.

The shortest distance r to which the ion and the molecule approach is given by the equations

$$bU = ru,$$

$$\tfrac{1}{2}\text{M}\,(u^2 - U^2) = \frac{\text{M}+m}{m}\,\text{R},$$

where u denotes the velocity of the ion in this position and b is the length of the perpendicular from the molecule to the rectilineal path of the ion.

We deduce

$$r^2 = b^2 \left\{ 1 + \text{R} \Big/ \tfrac{1}{2}\,\frac{\text{M}m}{\text{M}+m}\,\text{U}^2 \right\}^{-1}.$$

A collision will take place if

$$b^2 \leq \sigma^2 \left\{ 1 + \text{R}_\sigma \Big/ \tfrac{1}{2}\,\frac{\text{M}m}{\text{M}+m}\,\text{U}^2 \right\},$$

where $\sigma = \tfrac{1}{2}s' + \tfrac{1}{2}s$, the sum of the radii of the force spheres of the ion and molecule, and R_σ denotes the value of R at collision.

If R $= 0$, *i.e.*, if the polarisation of the molecule due to the ionic charge is negligible, the condition for a collision reduces to $b \leq \sigma$, as is otherwise obvious.

The connection between the velocity U and the mean thermal ionic velocity V can be deduced by the application of MAXWELL's law of distribution of velocities.   We obtain

$$\text{U}^2 = \text{V}^2 \left(1 + \frac{\text{M}}{m} \right).$$

Hence $\tfrac{1}{2}\dfrac{\text{M}m}{\text{M}+m}\,\text{U}^2 = \tfrac{1}{2}\text{MV}^2 = \tfrac{1}{2}mv^2$;   thus $\tfrac{1}{2}\dfrac{\text{M}m}{\text{M}+m}\,\text{U}^2$ is the mean kinetic energy of the molecular motion.

The effect of the polarisation due to the ionic charge is, therefore, as far as collisions are concerned, to replace σ^2 by $\sigma^2\,\{1 + 2\text{R}_\sigma/mv^2\}$.

Now the mean free path of an uncharged body of the same mass and dimensions as the ion is given by $\{\pi n\sigma^2\sqrt{1+\text{M}/m}\}^{-1}$, where n denotes the number of molecules per cubic centimetre.   Hence the actual mean free path of the ion is L, where

$$\text{I}^{-1} = \pi n \sqrt{1 + \frac{\text{M}}{m}}\,\sigma^2 \left\{ 1 + \frac{2\text{R}_\sigma}{mv^2} \right\}.$$

Expression for the Potential R *due to the Polarisation of the Molecule by the Ionic Charge.*—If the molecules of a gas are polarised by an electric field of intensity X, the electric moment per cubic centimetre is $\dfrac{K-1}{4\pi}X$, where K denotes the dielectric constant of the gas.   The electric moment (μ) of a molecule is therefore $\dfrac{K-1}{4\pi n}X$.

The mechanical force on the molecule is $\mu\,\dfrac{dX}{dr}$, which is equal to $\dfrac{K-1}{8\pi n}\dfrac{dX^2}{dr}$.   The potential is therefore given by

$$R = \frac{K-1}{8\pi n}X^2 = \frac{K-1}{8\pi n}\cdot\frac{e^2}{r^4},$$

when the molecule is polarised by the field due to the ionic charge.

This expression for R assumes that the polarising field is uniform throughout the volume of the molecule.   LANGEVIN (*loc. cit.*, p. 317) has obtained the general expression for R in the case of a spherical molecule and finds it to be given by a series of which the above is the most important term.

Expression for the Mobility of the Ion.—Let η denote the coefficient of viscosity of the gas, ρ its density, p the pressure in dynes per square centimetre, and l the molecular mean free path.   Let n_1, ρ_1, p_1, K_1 denote the values of n, ρ, p, K respectively corresponding to a temperature of $0°$ C. and a pressure of 760 mm. of mercury.

The charge e carried by the ion is taken as equal to that (E) on the monovalent ion in the electrolysis of solutions.   This equality was established from measurements of the mobility and rate of diffusion of gaseous ions.*   The exact value of the ionic charge is not required in the present treatment, inasmuch as e only enters in the expression $n_1e = n_1E$, which has been shown from experiments in electrolysis to have the value $1{\cdot}30 \times 10^{10}$,† E being measured in electrostatic units.   The product n_1E is denoted by A.

The gas is regarded throughout as being at a temperature of $0°$ C.

We have the following equations :—

$$k = e\mathrm{L}/\mathrm{MV}, \qquad \eta = \tfrac{1}{3}nmvl,$$

$$l^{-1} = \pi\sqrt{2}ns^2,$$

$$\mathrm{L}^{-1} = \pi n\,\sqrt{1+\frac{M}{m}\sigma^2}\left\{1+\frac{2\mathrm{R}_\sigma}{mv^2}\right\}, \quad \text{where} \quad \sigma = \tfrac{1}{2}s'+\tfrac{1}{2}s,$$

$$\mathrm{R}_\sigma = \frac{K-1}{8\pi n}\cdot\frac{e^2}{\sigma^4},$$

$$\mathrm{MV}^2 = mv^2 \text{ (equipartition of energy)},$$

$$e = \mathrm{E}, \qquad \rho = nm,$$

$$n_1\mathrm{E} = \mathrm{A}, \qquad p = \tfrac{1}{3}\rho v^2.$$

* *Vide* J. J. THOMSON, 'Conduction of Electricity through Gases,' 2nd edition, Art. 39.

† The electro-chemical equivalent of hydrogen was taken as $0{\cdot}00001035$ gram/coulomb.

We deduce the expression for the mobility in the form :—

$$k = \frac{A\eta}{\rho_1 p} \, 4\sqrt{2} \left(\frac{m}{M}\right)^{1/2} \left(1+\frac{M}{m}\right)^{-1/2} \left(1+\frac{s'}{s}\right)^{-2} \left\{ 1 + \frac{4(K-1)e^2}{\pi n m v^2 (s+s')^4} \right\}^{-1}.$$

When the mass and dimensions of the ion are the same as those of a molecule, we have $M = m$, $s' = s$, and the expression for the mobility becomes

$$k = \frac{A\eta}{\rho_1 p} \left\{ 1 + \frac{(K-1)e^2}{4\pi n m v^2 s^4} \right\}^{-1}.$$

This expression can be transformed into

$$k = \frac{A\eta}{\rho_1 p} \left\{ 1 + \frac{(K_1-1)\pi A^2 \eta^2}{2 p_1^2 \rho_1} \right\}^{-1}. \qquad \ldots \ldots \ldots (\alpha)$$

Consider the expression (α) which has been found for the velocity of an ion, regarded as a molecule carrying a charge equal to that associated with the monovalent ion in electrolysis, moving under unit electric intensity in a gaseous medium at a pressure p dynes per square centimetre and a temperature of $0°$ C.

For a given medium K_1, ρ_1, and p_1 are constant; whence k varies inversely as p, provided η is constant. Now, by MAXWELL's law,* the coefficient of viscosity of a gas is independent of its density; consequently over the range of pressures for which this law holds good we should expect the ionic mobility to vary inversely as the pressure, a conclusion which has been verified experimentally.

The expression (α) involves only known physical constants of the gas and is therefore directly comparable with the results of experimental observation. The results obtained by substituting the observed experimental values of the quantities involved are given in Table III. The values of the viscosity coefficients and of the dielectric constants have been taken from LANDOLT and BÖRNSTEIN's Tables (3rd edition); the constant p_1 was taken as 1,013,610 (dynes per square centimetre).

The sixth column in the table affords an indication of the effect on the mobility of the electric polarisation of the molecules due to the ionic charge; it will be seen that the effect is quite considerable. Column seven gives the values of the mobilities under a potential gradient of 1 volt per centimetre, which would be possessed by a molecule carrying a charge E if there were no retarding effect due to this polarisation. The remaining columns give the values of the mobilities as deduced from the expression (α) together with the observed experimental values of the positive and negative ionic mobilities; these values correspond to a real or hypothetical pressure of 760 mm. of mercury.

Unfortunately the values of K have been determined experimentally for only a very limited number of gases and vapours; in consequence, several vapours whose mobilities have been ascertained do not appear in the table.

* *Vide* JEANS, ' Dynamical Theory of Gases,' p. 252.

TABLE III.

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
							k_{760}.		
Gas or vapour.	Molecular weight.	$\rho_1 \times 10^5$.	$\eta \times 10^6$.	$(K_1 - 1) \times 10^5$.	$\dfrac{(K_1 - 1)\pi A^2 \eta^2}{2p_1{}^2 \rho_1}$.	$\dfrac{1}{300}\left(\dfrac{A\eta}{\rho_1 p}\right)$.	Calculated.	Observed.	
								+	−
							cm./sec.	cm./sec.	cm./sec.
Air	—	129	177	59	3·70	5·87	1·25	1·36	1·87
H_2	2	9	85	26	5·39	40·38	6·32	6·70	7·95
CO	28	125	163	69	3·79	5·58	1·16	1·10	1·14
N_2	28	125	163	59	3·24	5·58	1·31	1·6*	
O_2	32	143	191	54	3·56	5·71	1·25	1·36	1·80
CO_2	44	196	141	96	2·52	3·07	0·87	0·81	0·85
N_2O	44	196	141	107	2·80	3·07	0·81	0·82	0·90
NH_3	17	76	96	770	24·13	5·40	0·21	0·74	0·80
C_2H_6O	46	205	83	940	8·16	1·73	0·19	0·34	0·27
C_2H_5Cl	64·5	288	93	1554	12·06	1·38	0·11	0·33	0·31
$C_4H_{10}O$	74·1	330	69	742	2·77	0·89	0·24	0·29	0·31
CCl_4	153·8	686	153	426	3·76	0·96	0·20	0·30	0·31

* Mean value.

Considering that we are comparing the observed values of the mobility with absolute values calculated from various physical constants of the substances, the agreement is in several cases quite satisfactory; however, in the case of ammonia and the vapours there is a marked divergence between the calculated and observed values, the former being invariably smaller. The values of the dielectric constants for the vapours appear to be inordinately large, and, in this connection, it is interesting to note that it is also in the case of vapours that there is a marked departure from MAXWELL's law, $K = n^2$, where n is the refractive index. The following table will serve as an illustration :—

TABLE IV.

Gas or vapour.	K.	$K^{1/2}$.	n.
Air	1·000590	1·000295	1·000294
H_2	1·000264	1·000132	1·000138
CO	1·000690	1·000345	1·000340
CO_2	1·000960	1·000480	1·000450
N_2O	1·001070	1·000535	1·000500
NH_3	1·0077	1·0038	1·00037
C_2H_6O	1·0094	1·0047	1·00086
C_2H_5Cl	1·0155	1·0077	1·0010

In the case of MAXWELL'S law the reason for the departures is probably the existence in the molecule of free periods with durations long compared with that of the incident wave period.*   It is possible that, in the case under consideration, owing to free periods of long duration in the molecules of the vapours, these have not time to be completely polarised by the adjacent ionic charge during a collision.   It is worthy of mention that the large values of K which have been experimentally obtained for ammonia and vapours have been ascribed by some authorities† as being partially due to traces of conductivity which they possess.

Without dwelling further on the cause of these departures from the mobility law, it appears that, on the whole, the experimental values of the mobilities of the ions can be explained approximately on the supposition that the ion consists of a single molecule of the gas with which is associated a charge equal to that carried by the monovalent ion in electrolysis.   It has been shown from considerations based on the kinetic theory of gases that, irrespective of any theory as to the structure of the ion, the ascertained mobility values lead of necessity to the conclusion that the volume of the ion is in all cases greater than that of the corresponding gaseous molecule.   The question arises : what is the nature of this volume ?   On the one hand, if we neglect the influence of the charge on the mean free path of the ion, we are led to the conception of the ion as a cluster of molecules held together by forces arising from the polarisation due to the electric charge.   On the other hand, the effect of the charge on the collision frequency has been shown to be equivalent to an increase in the molecular sphere of force such that the resultant effective volume is sufficient to explain approximately the observed mobilities.   On this view the effect of the charge is to cause the ion itself and the neighbouring molecules to deviate from their rectilineal free paths ; SUTHERLAND,‡ by assuming such deviations to occur in the case of gaseous molecules by reason of attractive forces between them, was able to explain accurately the observed variation of the viscosity of gases with temperature.   LANGEVIN§ has obtained an expression for the ionic mobility by using the dynamical method employed by MAXWELL in the kinetic theory of gases ; he concluded that the experimental values of the mobilities lead to the necessity of regarding the ion as a cluster of molecules.   The question as to the nature of the volume of the ion as determined from the experimental mobility values could be decided if the ratios $\dfrac{e}{m}$ for the different gaseous ions were known.   In this connection it is worthy of mention that Prof. Sir J. J. THOMSON‖ has recently measured this ratio for the positive ions formed by cathode particles in oxygen at low pressures and came to the conclusion that the ion consisted of a single charged oxygen molecule.

*   *Vide* DRUDE, 'Theory of Optics,' Eng. trans., p. 389.
†   *Vide* BÄDEKER, 'Zeits. Phys. Chem.,' Bd. 36, p. 321, 1901.
‡   'Phil. Mag.,' vol. 36, p. 507, 1893.
§   'Ann. de Chim. et de Phys.,' vol. 5, p. 284, 1905.
‖   'Phil. Mag.,' vol. 16, p. 680, 1908.

Mention has already been made (*vide* section 8) of the increase in value of the product pk at low pressures in the case of air, nitrous oxide and carbon dioxide, and of the diminution in the case of vapours, *e.g.* ethyl chloride, when the pressures approach the vapour pressure at the temperature under consideration. Such deviations from the law $pk =$ constant could be ascribed to variations in the size of the cluster constituting the ion; however, they follow readily from the expression (α) of the mobility if we take into account the deviation from the law of MAXWELL which states that the coefficient of viscosity of a gas or vapour is independent of its density. In the case of gases it is known that η diminishes as the pressure is reduced beyond a certain value;[*] such a diminution would, according to the theory here given, produce an increase in the value of pk. In the case of vapours it has been established that η increases rapidly as the saturated state is approached; in fact, as a result of WARBURG and VON BABO's experiments on the viscosity of CO_2 at high pressures, MEYER[†] came to the conclusion that the experimental values above certain pressures could be explained only by supposing carbon dioxide to behave as a liquid, the density of which is practically independent of pressure; an increase in the value of η would, according to the expression (α), diminish the product pk, a result in accordance with experimental observations.

10. *Summary.*

1. The velocities of the positive and negative ions produced by Röntgen rays in 4 gases and 15 vapours have been measured at normal temperatures over a wide range of pressures and under different electric intensities. LANGEVIN's null method was employed throughout.

2. For a constant pressure the velocity of the ion was found to vary as the electric intensity.

3. It was found that, in general, the mobility (k) of the ion varied inversely as the pressure (p). In the case of nitrous oxide and carbon dioxide there was a slight increase in value of the product pk both for the positive and negative ions as the pressure was reduced below about 7 cm. of mercury. In the case of ethyl chloride there was a marked decrease in the value of pk as the vapour approached the saturated state; there is reason to believe that such a diminution would appear in the case of all the vapours in the neighbourhood of the saturated state.

4. In the case of vapours there was, in general, little difference in the values of the positive and negative mobilities. The mobility of the positive ion was found greater than that of the negative for aldehyde, ethyl alcohol, aceton, sulphur dioxide, ethyl chloride, pentane, ethyl acetate, methyl bromide, and ethyl iodide.

5. There appeared to be no direct relation between mobilities and molecular

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[*] *Vide* JEANS, *loc. cit.*, p. 253.

[†] *Loc. cit.*, Art. 90.

weights; the smaller mobilities invariably belonged to gases possessing high critical temperatures (the vapours); the larger mobilities to gases with low critical temperatures.

6. From the kinetic theory of gases an expression has been deduced for the mobility of an ion moving through a gaseous medium under the influence of an electric field. This expression takes into account the effect of the charge carried by the ion on its mean free path and involves only known physical constants of the gas.

7. As a result of the theoretical considerations it appears that the experimental values of the mobilities in the different gases at various pressures, as well as certain observed deviations from the law connecting the mobility and gaseous pressure, can be explained approximately on the supposition that the ion consists of a single molecule with which is associated a charge equal to that carried by the monovalent ion in electrolysis.

I take this opportunity of expressing my indebtedness to Mr. H. C. WILSON for setting up part of the apparatus; in conclusion, my thanks are due to Prof. THOMSON for the generous interest he has manifested in the research and to Prof. LARMOR for helpful advice.